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ITEM OF INTEREST

Prepared by

Science and Technology Section
Air Information Division

SUBJECT: Thermal Stability of Jet Fuels

SOURCES:

1. Davydov, P. I., and G. F. Bol'shakov. Effects of mercaptans on the formation of insoluble fuel sediment at elevated temperatures. Khimiya i tekhnologiya topliv i masel, no. 5, May 1961, 48-53. TP315.K44 1961. (S/065/61/000/005)

2. Davydov, P. I., and G. F. Bol'shakov. Effect of natural resins on the stability of jet fuels at elevated temperatures. Khimiya i tekhnologiya topliv i masel, no. 10, Oct 1960, 35-38. TP315.K44 1960. (S/065/60/000/005)

3. Bespolov, I. Ye., D. Ye. Kestner, and O. V. Pletneva. The catalytic effect of copper-base alloys on resin formation in T-type jet fuels. Khimiya i tekhnologiya topliva i masel, no. 9, Sep 1957, 66-70. TP315.K44 1957. (S/065/57/000/005)

A study of the effect of mercaptans on the formation of insoluble sediment in jet fuels at elevated temperatures is reported [1]. The method of investigation consisted essentially in the heating of sealed samples of the fuels in glass containers in the presence of a continuously rotating 10-cm² plate made of BB-24 bronze [2]. In addition to copper [and probably other unspecified components], this alloy contains 5.7% antimony and 0.9% phosphorus and exerts a strong deteriorating effect on jet fuels at elevated temperatures [3]. The effect decreases upon introduction of nickel and zinc and reduction of phosphorus content to 0.2% [3].

The study was conducted in three experimental series. Series 1 involved the testing of TC-1 fuels to determine the temperature of maximum sediment formation. The fuels were products of a variety of Second Baku crudes, and their mercaptan sulfur content was from 0 to 0.0211%. The method described above [2] was employed in the 100 to 300°C range. Specimens were held at temperature for six hours.

Series 2 dealt with the effects of mercaptans and catalytic metals on sediment formation at 150°C in a specially hydrofined TC-1 fuel. (After hydrofining, the fuel, a product of a Tuymazy crude, is mercaptan-free with total sulfur content of only 0.011%.) The experiments were conducted with the fuel in this initial state and with additions of increasing amounts of two specially synthesized mercaptans, sec-octylmercaptan and thiophenol, to the fuel. The experiments took place a) in glass containers with no catalytic metals present, b) in glass containers also containing the BB-24-bronze plate, and c) in a brass container also containing the plate. Again, specimens were held at temperature for 6 hours.

Series 3 extends the experiments of series 2 to the 100-300°C range.

The following are the findings of the investigation:

In series 1 sediment formation increased with increasing mercaptan content, and the temperature of maximum sediment formation was 150°C.

In series 2 no sediment was formed in the mercaptan-free fuel heated in the glass container with no bronze plate present, small amounts of sediment formed in the presence of the metal, and the amount of sediment increased when the brass container was used. Additional amounts of either mercaptan with no metal present increased the sediment. Thiophenol exerted a stronger effect than sec-octylmercaptan in this case; e.g., at 0.020% mercaptan sulfur content the presence of thiophenol produced 6.5 mg/100 ml of sediment compared to only 0.8 for sec-octylmercaptan. When the metal was brought into contact with the fuel, the results were reversed. The values were 5.0 for thiophenol and 14.5 for sec-octylmercaptan. Introduction of the brass container reduced the amount of sediment under otherwise identical conditions to 3.0 and 11.0 mg/100 ml, respectively.

The metals, however, were corroded by the mercaptans, especially thiophenol, which formed loose rough films on the bronze surfaces. The decrease in sediment in the brass containers is explained by the partial transition of mercaptans into the corrosion film. The formation of sediment remained on a level of 2.4 to 3.0 mg/100 ml in the experiments employing the brass container and the bronze plate with 0 to 0.020% thiophenol added to the mercaptan-free fuel.

The results obtained in series 3 confirmed that maximum sediment formation also takes place at 150°C under all the conditions of the experiment.

In experiments in the glass container in which mercaptans were added to the mercaptan-free low-sulfur fuel and the bronze plate was present, the sulfur balance after sediment formation indicated that the mercaptans partly oxidize, partly form sediment, and partly take part in the metal-corrosion process. With 0.01% thiophenol sulfur more corrosive sulfur--3.49 mg/100 g (0.39 in the sediment, 6.4 remaining in the form of mercaptans in the solution, and 6.7 in the corrosion film)--was found by analysis after the experiment than was initially introduced in mercaptan form (i.e., 10 mg/100 g). The corresponding balance with mercaptan-free fuel indicated no sediment at all in the absence of the bronze plate and sediment with very small amounts of sulfur (0.002 mg/100 g, which is negligible) in the presence of the plate and no corrosion on the bronze. These findings indicate that non-mercaptan sulfur becomes corrosive in the presence of thiophenol.

Analysis of sediment of mercaptan-containing fuels (0.01%) obtained in the glass container in the presence of the bronze plate showed considerable ash content, about 12%. The ash contained Cu, Zn, and Cr in amounts from 1 to 10% and smaller amounts (down to 0.001%) of Ca, Fe, Ni, Se, Al, Mg, Mn, Pb, Sb, Sn, and Ba. Ash from thiophenol sediment contained iron in amounts from 1 to 2%. Sieve analysis of particles formed with either mercaptan indicated that the majority of sediment particles was retained on the 5-7-micron and 15-micron sieves. Mercaptan-free fuels produced smaller sediment particles.

COMMENT:

This study indicates the continuation of Soviet efforts in the investigation of sediment formation in TC-1 fuel and in the search for a standard method of evaluating the thermal stability of this fuel. The role of mercaptans in fuel deterioration at elevated temperatures is confirmed.

The catalytic effect of such copper alloys as BB-24 and brass would seem to be of particular concern to the Soviets, since provision was made for its introduction as a condition of the testing procedure. The comparatively high ash content of the sediment with the presence of metals in amounts ranging from a few percent of total ash content to merely traces is comparable to that of the sediment found in TC-1 fuels at lower temperatures under conditions of actual flight. (See: AID

Report 61-100, 7 Jul 1961.) This fact appears to be in li
with the observation put forward in the commentary to AID
port 61-100 that wear and corrosion sludge could possibly
ert a catalytic effect on sediment formation.

The presence of Zn and Cr in the ash portion of sediment in amounts from 0.3 to 10% is to be noted because source [2] mentions only Sb and P as components of Б5-24 bronze.

The specially hydrofined TC-1 fuel used in the p
ent study is reported as a mercaptan-free material. This
cumstance and some data also used in the study on the merc
content of nonhydrofined TC-1 fuels justify some comments
the question of hydrofining of TC-1 fuels of Second Baku o
The TC-1 specification, ГОСТ 7149-54, permits a maximum o
0.01% mercaptan sulfur, with total sulfur content not to e
ceed 0.25%. In the present experiments a marked degree of
iment formation took place in the TC-1 fuels at mercaptan
total sulfur contents far below the amounts prescribed by
specification. (e.g., sediment formation, approx. 4-7 mg/
at 150°C; respective mercaptan and total sulfur contents,
0.0051 and 0.146% [Tuymazy and Ishimbay] and 0.0072 and 0..
[Mukhanova].)

It was noted above that nonmercaptan sulfur bec
corrosive when the aromatic mercaptan, thiophenol, was pre
in the fuel. If considerable amounts of sediment form in
transport jet aircraft at 45-50°C (AID Report 61-100), the
more sediment can be expected to form when the jet fuel is
in the capacity of an engine coolant subject to the presen
of catalytic metals in other types of jet aircraft. There
though the authors of the article refrain from any comment
other than on the desirability of taking the differences i
sediment formation into account in the development of a st
ard method for evaluating thermal stability, the study may
well be considered further evidence in support of the cont
plated introduction of hydrofining for Second Baku jet fuel
(For information on the desulfurization of jet fuel by hyd
fining see also: AID Report 61-26, 7 Mar 1961.)